

MANUFACTURE OF WOOD–CEMENT COMPOSITES FROM *ACACIA MANGIUM*: MECHANISTIC STUDY OF COMPOUNDS IMPROVING THE COMPATIBILITY OF *ACACIA MANGIUM* HEARTWOOD WITH PORTLAND CEMENT

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ABSTRACT

Numerous inorganic compounds were screened to identify those capable of minimizing the inhibitory effect of *Acacia mangium* heartwood on the setting of cement. It was hypothesized that the most effective compounds would be ones that could accelerate the hydration of cement and form complexes with inhibitory phenolic extractives found in the heartwood of *A. mangium*. Our hypothesis proved correct since compounds such as SnCl₄, AlCl₃, and FeCl₃ and/or their ionic species that were able to bond with the phenolic heartwood constituents of *A. mangium* as well as accelerate cement hydration were generally more effective at strengthening cement hydration in the presence of *A. mangium* heartwood than compounds that simply accelerated cement hydration. Compounds containing Ni²⁺, Ag⁺, Fe³⁺, and Co²⁺, that bonded to phenolic constituents of *A. mangium* heartwood, but lacked the ability to strongly accelerate cement hydration increased maximum hydration temperature attained in wood–cement mixes. The findings suggest that complexation of phenolic heartwood extractives may be an important mechanism by which inorganic compounds reduce the inhibitory effect of certain wood species on the hydration of cement. A combination of compounds including a cost-effective accelerator (such as CaCl₂ or MgCl₂) and an efficient chelating agent (containing such ions as Al³⁺, Sn⁴⁺, or Fe³⁺) may have considerable synergistic effects and could potentially enable wood cement composites to be manufactured from *A. mangium*.

Keywords: Cement hydration, *Acacia mangium*, heartwood, phenolic extractives, wood–cement boards, complexes.

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INTRODUCTION

Tropical hardwoods such as *Acacia mangium* (Willd.) are increasingly important plantation species in S.E. Asia most notably in Indonesia, where large areas of natural forest are being converted into industrial plantations (Vercoe 1993). Plantations of *A. mangium* are being developed primarily to supply the pulp and paper industry, but there is on-going interest in using the wood for the manufacture of composite panels including wood-cement composites (Abdul-Kader and Sahri 1993).

Certain wood species are unsuitable for the manufacture of wood-cement composites because they contain low molecular weight extractives that inhibit the hydration and setting of cement. Notable in this regard are western larch (*Larix occidentalis* Nutt), which contains large quantities of water-soluble arabinogalactan, (Hofstrand et al. 1984; Zhengtian and Moslemi 1985) and many tropical hardwoods that contain high levels of heartwood polyphenols (Sander-mann and Kohler 1964).

The inhibitory effects of wood extractives on the setting of cement can be reduced by chemically accelerating cement hydration, thereby minimizing the exposure of the cement gel to low molecular weight compounds diffusing from wood. Accordingly, simple inorganic compounds are commonly added to wood, or cement, to accelerate cement hydration and improve properties of wood-cement composites (Kayahara et al. 1979). CaCl_2 has long been favored commercially as a cement setting accelerator due to its effectiveness, low cost, and availability (Lea 1971); however, it appears to be ineffective at countering the inhibitory effect of phenolic extractives from the heartwood of *Acacia mangium* on cement hydration (Tachi et al. 1988). Finding a solution to the problem of the inhibitory effect of *A. mangium* heartwood polyphenols on cement hydration would open up the possibility of manufacturing wood-cement composites from *A. mangium*, without the need to remove extractives from wood (by water soaking) before mixing it with cement.

It is well known that simple phenols and plant polyphenols can be oxidatively polymerized by

metals (Haslam 1966; Mihailovic and Cekovic 1971). The formation of insoluble complexes could reduce the inhibitory effect of phenolic wood extractives on cement hydration by blocking hydroxyl groups and/or reducing the rate at which the polymerized extractives can diffuse from wood into the curing cement gel. If this hypothesis is correct, then inorganic compounds with the ability to coordinate and polymerize phenolic extractives and accelerate cement hydration should be more effective than simple accelerators such as CaCl_2 at improving the properties of wood-cement composites manufactured from *A. mangium*.

In this work, we screened large numbers of inorganic compounds to determine the extent to which they were able to accelerate the hydration of cement, coordinate phenolic extractives, and minimize the inhibitory effect of *A. mangium* heartwood on the setting of cement. The aim was to test the aforementioned hypothesis in order to select the most effective compounds to use as additives during the manufacture of wood-wool cement boards from *A. mangium*.

MATERIALS AND METHODS

Wood sample collection and preparation

Wood-wool was obtained from two 8-year-old Brown Salwood (*Acacia mangium* Willd.) trees grown in provenance trials at Damper (18°24'S, 146°06'E, altitude 20 m asl) in North Queensland, Australia. Two end-matched logs, 1.15 m long, were removed from the felled trees. Two end-matched billets, 0.46 m long, were cut from the middle of each log. The eight billets were shredded in the green condition into wood-wool strands measuring $0.3 \times 3 \times 460$ mm, keeping the wood-wool from the two trees separate. The wood-wool was air-dried under cover for 2 weeks and grab-samples (approx. 100 g) were then selected at random and sorted by color to isolate and retain strands of pure heartwood. The heartwood strands were cut into pieces approximately 50 mm in length using scissors, and stored for at least 2 weeks in a conditioning

room maintained at $20 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ r.h., until needed.

Compounds and their preparation

In total, 137 inorganic compounds were tested. These comprised chlorides, sulphates, nitrates, acetates, oxides, carbonates, and fluorides of Ag^+ , Al^{3+} , Ba^{2+} , Ca^{2+} , Co^{2+} , Cr^{3+} , Cu^+ , Cu^{2+} , Fe^{3+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Sr^{2+} , Zn^{2+} , and Zr^{4+} . Several miscellaneous compounds including citrates, tartrates, bromides, and oxalates of Na and K were also assayed. The solubility in water (at room temperature $\sim 20^\circ\text{C}$) of each compound was checked (Weast 1970) to determine whether to add them to cement as a solid or liquid. The water-soluble compounds were first dissolved in distilled water at room temperature to 0.1 M strength in a 250-ml volumetric flask. Four 40-ml aliquots of the compound solution were poured into separate 50-ml capacity vials for addition to cement hydration samples: two for addition to wood-cement samples and two for addition to samples containing cement only. The two vials allocated to wood-cement samples were prepared with an extra 0.7 ml of distilled water per g of wood used, in accordance with the recommendations of Hachmi et al. (1990).

Those compounds insoluble in cold water were pulverized using a mortar and pestle, and four equal amounts were weighed out into four 5-ml capacity vials for addition as a dry powder to cement hydration samples. The amount of each compound used in a hydration test corresponded to the amount that would be present in 40 ml of a 0.1 M solution if the compound were soluble in water. This ensured consistency in concentration of additives across soluble and insoluble compounds.

Measurement of cement hydration exotherms

An aliquot of compound solution was added to a 100-g sample of fresh dry Portland cement Type I (Blue Circle Southern brand, batch no. 090MA99) in a sealable "Dalgrip" polyethylene bag and thoroughly mixed by hand kneading for

about 2 min at 20°C . Insoluble compounds were added as a dry powder to 100 g of dry cement in a 'Dalgrip' bag and evenly tumbled through the cement, after which distilled water was added to mix the cement slurry as described above. For samples containing only pure cement or cement plus compound, but no wood, 40 ml of distilled water or compound solution was added. For each cement sample to which wood was to be added, 43.5 ml of distilled water or compound solution was first added and mixed. Five g of chopped *A. mangium* heartwood-wood was then added and massaged through the cement slurry until strands were evenly coated. Immediately after the mixing of a cement hydration sample, the heat liberated by the sample was measured using a thermocouple (Type J) attached to a temperature logging apparatus, as described previously (Semple and Evans 2000). Six wood-cement samples were measured at a time over a 23-h period. Temperatures were recorded at 15-min intervals. The curves were smoothed by plotting the progressive average of each three successive readings. Maximum heat of hydration temperature (T_{max}) and time taken to reach T_{max} (t) were recorded, and a wood-cement compatibility index, hydration rate (R) = $(T_{\text{max}} - T_{\text{min}})/t$, was calculated. The T_{min} component of hydration rate is the minimum temperature attained during the first 5 h of hydration. All experiments were done in a controlled temperature room maintained at $20 \pm 1^\circ\text{C}$.

Experimental design and statistical analysis

In addition to the two cement controls (cement only) and two wood-cement control samples, 137 compounds were tested, with two replicates for pure cement and two replicates (trees) for wood-cement samples. The experimental design contained a nested structure of cement and cement + wood hydration samples within the compounds' stratum. In each daily six-replicate run of hydration samples, three compounds were tested at random. For each compound, two matched samples were run, one with cement + compound and the other with cement + compound + wood. All compounds were run in random order for replicate 1 (cement) and wood

from tree 1 (cement + wood) over the first 46 days followed by replicate 2 and wood from tree 2, again randomized by compound over the next 46 days. The effects of two fixed factors, compound and its solubility in water, were tested using an appropriate mixed ANOVA model at the 5% significance level. Compounds were ranked in order of their efficacy in improving the strength (expressed as T_{\max} and hydration rate) of the exothermic reaction of cement containing the inhibitory heartwood-wool of *A. mangium*. Compounds were also assessed for their effects on the normal course of hydration of Portland cement by comparing T_{\max} and hydration rate of cement containing compound with those of cement alone.

Determination of polyphenol–metallic complexes

Sodium hydroxide was used to obtain a leachate containing alkali-soluble inhibitory polyphenols from *A. mangium* heartwood. To obtain the heartwood leachate, 10 g of chopped *A. mangium* heartwood wool was placed in a beaker containing 300 ml of solution at pH 11.5–12 (0.01 M NaOH) and soaked in a water bath for 6 h at 30°C. After soaking, the wood-wool was removed, and the leachate was filtered under vacuum through a 40-mm-diameter sintered glass crucible (frit no. 3) to remove any sludge and solids such as wood fiber. Then 100 ml of the dark leachate was diluted with 150 ml of 0.01 M NaOH to produce a transparent brown liquid in which any insoluble precipitate resulting from the addition of a particular additive could be clearly seen. A small amount (1 ml) of 0.1 M solution containing a soluble additive compound was added to 7 ml of the dilute alkali leachate in a glass vial to test its ability to form an insoluble complex with heartwood polyphenols in alkaline medium.

RESULTS AND DISCUSSION

Compound ranking

The 20 compounds that resulted in the greatest increase in hydration rate for cement containing

A. mangium heartwood strands were all water-soluble and are listed in Table 1. Several compounds were significantly more effective than CaCl_2 at increasing cement hydration in the presence of *A. mangium* heartwood. The top six compounds that increased hydration rate (R) beyond 3°C/h were SnCl_4 , AlCl_3 , FeCl_3 , $\text{Zr}(\text{NO}_3)_4$, $\text{Al}(\text{NO}_3)_3$, and MgCl_2 . The capacity of each compound to precipitate *A. mangium* heartwood polyphenols is ranked from 0 (no precipitate) to 5 (very strong precipitate formed within seconds). In accord with our suggested hypothesis, all compounds in the top six except for MgCl_2 (6th) strongly interacted with *A. mangium* heartwood tannins by forming an insoluble precipitate in alkaline medium. CaCl_2 , which formed a weak precipitate, was ranked 13th in terms of hydration rate, lower than two other compounds that did not precipitate heartwood tannins including MgCl_2 and BaCl_2 .

TABLE 1. The 20 most effective compounds ranked by hydration rate attained in wood–cement mix, with corresponding maximum hydration temperature, time, and the strength of precipitate formed with alkali soluble *A. mangium* heartwood extract.

Compound	Hydration rate (°C/h)	Max. Temp. (°C)	Time (h)	Precipitate*
SnCl_4	5.3	59.9	6.9	5
AlCl_3	4.5	53.6	6.9	5
FeCl_3	3.6	51.5	8.1	5
$\text{Zr}(\text{NO}_3)_4$	3.5	54.6	7.2	5
$\text{Al}(\text{NO}_3)_3$	2.9	48.4	6.4	4
MgCl_2	2.8	48.9	9.5	0
BaCl_2	2.6	47.2	9.4	0
NiCl_2	2.5	46.6	9.2	4
$\text{Al}_2(\text{SO}_4)_3$	2.3	48.5	8.9	4
$\text{Fe}(\text{NO}_3)_3$	2.3	47.3	8.9	4
SrCl_2	2.1	47.1	10.0	0
CaCl_2	2.1	45.4	9.9	1
PbCl_2	2.1	46.0	22.9	5
Na_2CrO_7	2.0	47.8	11.4	4
$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$	1.9	46.6	11.0	3
$\text{Co}(\text{NO}_3)_2$	1.9	44.2	13.9	4
AgNO_3	1.9	47.4	11.6	4
Cr_2O_3	1.8	45.7	11.4	4
$\text{Ba}(\text{NO}_3)_2$	1.8	43.4	10.4	0
$\text{Ca}(\text{NO}_3)_2$	1.7	44.6	10.7	0
Wood Control	0.5	31.0	18.5	

*0 none, 1 very slight precipitate, 2 weak, 3 moderate, 4 strong, 5 very strong.

In studies by Zhengtian and Moslemi (1985) and Wei et al. (2000), 30 compounds, mainly chlorides, nitrates, and sulphates, were tested for their effects on the hydration of Portland cement containing western larch heartwood flour and birch (*Betula albosinensis* Burke.) flour, respectively. The most effective compounds for ameliorating cement inhibition identified by both studies were the chlorides, SnCl_2 , FeCl_3 , AlCl_3 , and CaCl_2 . Our findings accord well with theirs except in the performance of CaCl_2 . This discrepancy may be explained by the fact that these workers used woods that do not contain tannin polyphenols.

Figures 1 and 2 illustrate the distribution of different compounds according to their effect on the hydration of pure cement and cement containing heartwood strands. Their effects on T_{max} (Fig. 1) and hydration rate (Fig. 2) are graphed for pure cement + compound (x -axis) and the wood + ce-

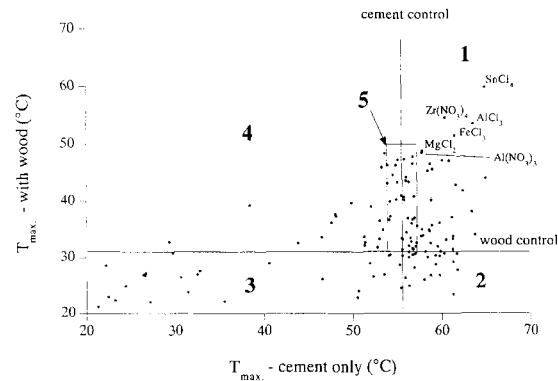


FIG. 1. T_{max} for cement containing compound only vs T_{max} for cement containing compound plus wood-wool. T_{max} for pure cement (cement control) and for cement containing wood only (wood control) is indicated by lines.

ment + compound mix (y -axis). The results clearly show that the most effective compounds for ameliorating the inhibitory effects of A.

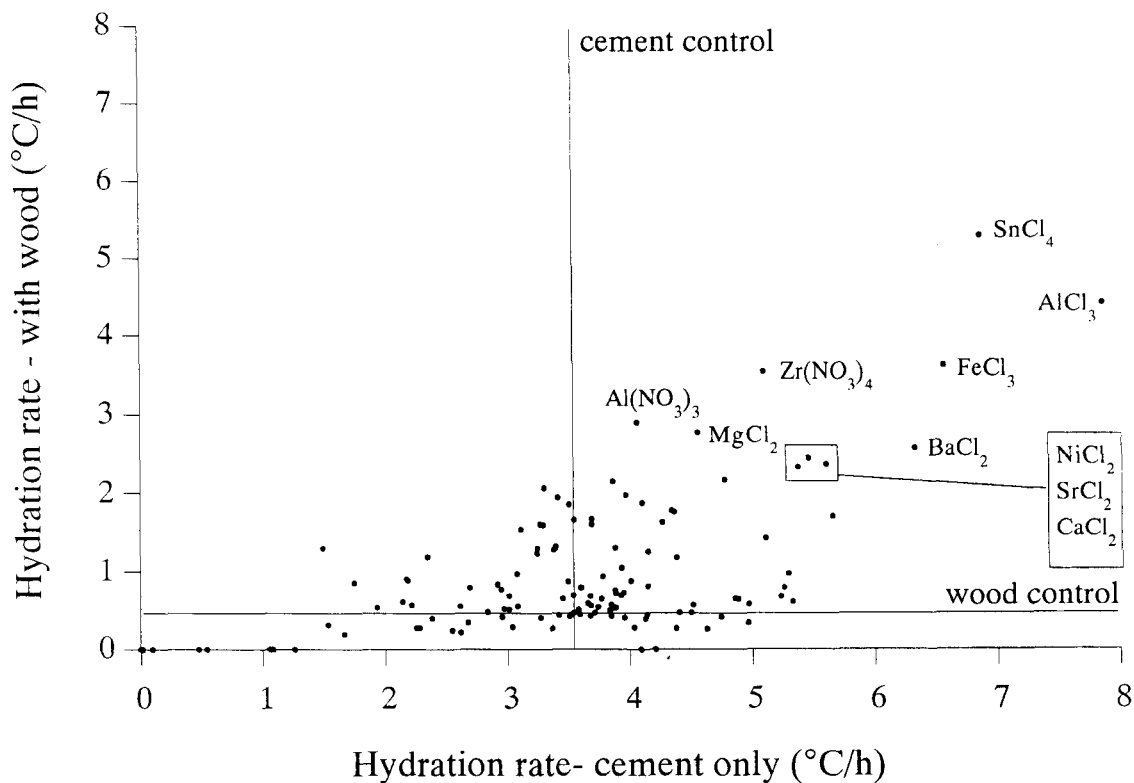


FIG. 2. Hydration rate for cement containing compound only vs hydration rate for cement containing compound plus wood-wool. Rate for pure cement (cement control) and for cement containing wood only (wood control) indicated by lines.

mangium heartwood were also those that produced the greatest increases in maximum hydration temperature and rate of hydration in pure cement.

Figures 1 and 2 also show the interactive effect of the inorganic compounds and the presence or absence of wood on T_{\max} (Fig. 1) and hydration rate (Fig. 2) of cement. Compounds in quadrat 1 (on Fig. 1) increased T_{\max} and hydration rate in both pure cement and cement containing wood. Almost all compounds that increased the maximum temperature and rate of hydration in the wood-cement mix accelerated the hydration of pure cement as well, and indeed the top six were also those with the greatest accelerating effect on pure cement. Compounds in quadrat 2 had their positive effects on the hydration of pure cement nullified by the presence of inhibitory *A. mangium* heartwood (Fig. 1). Such compounds included NaCl, Na_2SO_4 , and KBr; these are compounds which when added in small amounts accelerate cement hydration to some degree (Lea 1971), but whose action was not strong enough to counteract the inhibitory effects of the wood. Compounds that reduced T_{\max} and hydration rate (quadrat 3) contained inhibitory cations i.e., Cu^+ , Cu^{2+} , Pb^{2+} , Co^{2+} , Zn^{2+} , and Mn^{2+} , or citrates and tartrates. Compounds in quadrat 4 reduced T_{\max} of pure cement, but increased T_{\max} of wood cement mixtures. A fifth group of compounds (enclosed on Fig. 1) had little effect on T_{\max} of cement on its own, but increased the temperature and hydration rate attained in cement containing heartwood. These included nitrates and acetates of Al^{3+} , Ni^{2+} , Ag^+ , Fe^{3+} , and Co^{2+} , compounds that had little accelerating effect on the hydration of pure cement. All these compounds caused the formation of precipitate with *A. mangium* heartwood tannins in alkaline medium.

The results provide evidence to suggest that the formation of insoluble polyphenol-metallic complexes between free cationic species and reactive hydroxyl sites on heartwood polyphenols contributes to ameliorating the inhibitory effects of *A. mangium* heartwood. Our findings indicate that chlorides and nitrates containing cations with a higher positive charge (such as Sn^{4+} , Zr^{4+} , Fe^{3+} or Al^{3+}) are the most effective addi-

tives. Although cost would preclude the use of zirconium compounds; accelerators based on tin, iron, or aluminium may be far better suited than CaCl_2 for use in wood-cement composites containing *A. mangium* and possibly other tropical hardwoods that contain high levels of heartwood polyphenolic extractives. Other studies have also found compounds containing aluminium to be more effective than CaCl_2 for ameliorating the inhibitory effects of hardwoods used in the manufacture of wood-cement composites. For example, AlCl_3 was found to be the most effective chloride compared with MgCl_2 , FeCl_3 and CaCl_2 for the manufacture of wood-cement composites from the inhibitory wood of *Shorea* spp. (Kayahara et al. 1979). $\text{Al}_2(\text{SO}_4)_3$ is a more effective additive than CaCl_2 for manufacturing WWCB from pre-soaked *A. mangium* wood (Soriano et al. 1998). These studies did not consider reasons as to why this might be the case.

Interaction with heartwood polyphenols

Water and alkali-soluble heartwood tannins have deleterious effects on cement hydration, as has been demonstrated experimentally by Sandermann and Brendel (1956) and Miller and Moslemi (1991). These studies indicate that the addition of more than about 0.2% will effectively inhibit cement hydration. Condensed tannins can be abundant in the heartwood and bark of acacias (Sherry 1971; Hillis 1987). Their molecules contain *o*-dihydroxyphenyl groups, which have excellent chelation affinity with free metal ions including Cu^{2+} and Zn^{2+} (McDonald et al. 1996; Yamaguchi and Okuda 1998), Fe^{3+} and Al^{3+} (Kennedy and Powell 1985; Yoneda and Nakatsubo 1998). In our study, solutions containing free cations, or more likely cationic hydrated and oligated species based on Sn^{4+} , Al^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+} , all formed strong precipitates with the dark-colored polyphenols leached from *A. mangium* heartwood in alkaline solution leaving a light yellowish or clear solution behind. Although the interactions between a cement hydration accelerator such as SnCl_4 or FeCl_3 , its aqueous dissolution products, and dissolved polyphenols of

